

Alloys as Solutions

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ALLOYS AS SOLUTIONS

BY JOHN ALEXANDER MATHEWS

It is truly remarkable that any class of substances which have been so long known and studied as the alloys have been should have hidden the secrets of their inner molecular constitution so completely until within a little more than a decade. The art of metallurgy is a venerable one, and wonderful achievements were accomplished by the earliest civilized peoples in practicing metallurgy as an empirical art and with the crudest of appliances. The Chinese are supposed to have had metallic currency for at least 4,000 years; the Lydians depicted nymphs, deities and animals upon metallic coins in the eighth century B. C., and the coins of Greece dating 300 B. C. show a skill of workmanship not excelled by modern engravers. We may, from these evidences of the advances in civilization, conclude that the knowledge of metals and how to obtain and utilize them was of very early origin.

Historical Review.—Six metals are mentioned in the Old Testament scriptures, and from this and other sources we know that brass, bronze, solders and other alloys were all well known before the Christian era. We have records of the metallurgical processes of cupellation, amalgamation and smelting of an equally early date. During all the centuries from that time to the present, men have been discovering new metals and mixing them in new proportions hoping either by design or chance to produce improved materials suitable for special purposes. The shrewd observers of all ages seem to have been aware of the profound changes which the properties of metals undergo

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when mixed; even though one metal may be added in but minute quantities the result is often practically a new metal, and to these early students these were considered in very truth new metals. The ancients did not recognize brass as an alloy. They only knew that when copper was melted with a certain earth (zinc ore) it became more yellow and golden in appearance. This single experiment no doubt had much to do with the development of the alchemistic idea of the transmutability of metals. It must be remembered that although the speculative philosophy of the ancient Greeks did much to hinder the development of modern scientific methods and imposed strong opposition to physical research, yet it did much to stimulate thought about natural law. The teachings of Aristotle and Plato must certainly have inculcated a deep feeling of respect for the dignity of science, but this spirit was held in check for many centuries by reason of the evolution of the rigid dogmatism of the Christian era. Encouraging signs of improvement in the way of a revival of learning during the time and through the influence of Alfred the Great were offset by the more than equal revival in ecclesiasticism at the same period.

The work of two or three men left a lasting impression upon scientific metallurgy in spite of all opposition. Geber, in the eighth century, and Agricola and Biringuccio, in the fifteenth century, recorded many discoveries as the results of their studies and experiments upon the properties of metals. These men, who were in advance of their times, lived during the days when the church heaped contempt upon all investigations of nature because of a belief in their futility. Men of inquiring minds had to work in secret, and thus the belief in the occult, magic and witchcraft were mightily stimulated. These were the days when papal bulls still roared that the earth was not round, because in Holy Writ the "corners of the earth" are mentioned. But even after the domination of scholasti-

cism had in great part ceased, no one seems to have advanced any idea as to the nature of metallic alloys. Oxidation and reduction had long been subjects for study, and one of the very earliest of the Royal Society's investigations was into the cause of the gain in weight of lead when heated in air, and it was discovered that it was due to the absorption of some constituent of the atmosphere. It is not strange that this problem attracted such early attention, for the behavior of lead in the fire had been utilized in the refining of gold and silver for sixteen hundred years and cupellation for the sake of quantitatively determining the richness of gold and silver alloys had been used in England from the time of Roger, Bishop of Salisbury, in the reign of Henry I, to whom Du Cange, the historian, gives the credit for "inventing" assaying. The bad practices in which the coiners of money had engaged during the times of William the Conqueror and his son, Rufus, were thus corrected by Henry, and of fifty coiners examined by Roger only four escaped punishment.

In the phlogistic period, which may be said to comprise the end of the seventeenth and most of the eighteenth centuries, metallurgy made some decided advances. Bergman advanced an explanation of the distinctions between wrought iron, cast iron and steel as early as 1781, and even stated the percentages of carbon (which he called phlogiston) that each class contained. Still earlier than this, Réaumur (1722) explained the hardening of steel by assuming that the metal was constituted of particles which might be likened to piles of shot. These particles contained "sulphur and salts," which, by reheating, were driven into the interstitial spaces, and by quenching the cooling was so quick that they could not get back into the molecule. At the end of the eighteenth century the discussion of free or combined carbon had begun; Cloët carbonized iron by means of a diamond in 1798; and a year later it was stated that carbon and iron form

a true chemical compound. Notwithstanding these great advances, no very decided opinions upon the constitution of intermetallic mixtures seem to have been recorded.

One could scarcely expect that the hard problems of molecular physics, which a study of alloys involves, would be solved before the announcement of a molecular theory of the constitution of matter, nor could it have made any progress before the period of chemical reform begun by Lavoisier, the period of quantitative investigation. But only recently, even in this period in which we still labor, have the relations of physical properties to chemical constitution attracted both chemists and physicists to concerted activity, and in this field of investigation alloys were last to yield fruitful results. Physical and chemical methods of research, which were entirely satisfactory when applied to bodies of other kinds, failed utterly to afford a rational explanation of the molecular conditions existing in alloys. The solution of these problems required new methods and new apparatus. Fortunately, these are at hand; they have been slowly evolving and the past decade has been most fruitful of results. Problems of the greatest practical importance and of extreme difficulty have been solved. Yet much remains to be done, as we have but entered upon this new field of applied science. Let us review the work so recently accomplished by a host of investigators which, I am sorry to say, does not include many Americans. We have not done our part in this work, for, with few exceptions, the great leaders in it belong to the school of English and French physicists, chemists and metallurgists. A resumé of their achievements may be of interest at this time, and this is given in the pages that follow.

A most potent factor in this recent progress has been the official recognition of the necessity of study along these lines. More than ten years ago the Institution of Mechanical Engineers of Great

Britain appointed an Alloys Research Committee, which receives financial assistance from the institution, and five reports have been published by it, and a sixth report is, I believe, about to appear. It is in connection with the work of this committee that Sir William Robert-Austen, his pupils and the co-workers of his staff have produced such excellent work, especially in pyrometry and in explaining the complicated changes, allotropic and otherwise, which steel and cast iron undergo. The practical operations of annealing, tempering, hardening, etc., can now be conducted upon a scientific and rational basis. The effects of thermal operations can be predicted accurately and desired results obtained unfailingly. It would be too much to say that all this is due to this committee alone; but if we include also the committee of the British Association, appointed to investigate the nature of alloys, of which Mr. Neville is chairman and the "Commission des Alliages," of the Societe d'Encouragement l'Industrie Nationale, as also sharing the honors of recent great advances in both our theoretical and practical knowledge of alloys, then we have recognized the three most prolific contributors to our knowledge of metallic mixtures. While giving these official bodies full credit for their discoveries, we would not detract in any way from the honor due to many individual workers not connected with committees who are scattered through many lands. It is safe to say, however, that the larger results of the concerted work of committees has had a stimulating effect upon the private worker. One of the greatest evidences of appreciation of the necessity for research in connection with alloys is that nearly every railroad in France and many metallurgical concerns contributed to sustain the work of the "Commission des Alliages."

The purely scientific reasons which have made possible the recent advances in alloys research seem to me to be : (1) *An increased knowledge of solutions.* For this we are undoubtedly indebted

in very great measure to the great Dutch and German physical chemists—Vant Hoff, Roozeboom, Ostwald, Nernst and others. (2) *The development of metallography*. This seems to have originated with Dr. Sorby, of Sheffield. Although he wrote about the microstructure of meteoric iron as early as 1864, the progress of metallography was very slow. Only within the past ten or fifteen years have even metallurgists begun to recognize what a valuable aid to research it is and unfortunately the manufacturers have not yet given it just recognition. Recent progress in this branch of applied sciences is most closely attached to the names of Stead, Martens, Osmond, Le Chatelier, Charpy, Roberts-Austen, Howe and Sauveur. (3) *Improvements in pyrometry*. The study of metals, alloys, furnace reactions, etc., was retarded for many years because of the lack of the suitable means of measuring accurately very high temperatures. Such means as have been available for these purposes in past years were not suitable for general use around shops and metallurgical works and were inconvenient even for the laboratory. Now, however, there are at least two reliable pyrometers which are conveniently manipulated and lend themselves readily to accurate measurements of high temperatures. The Siemens electrical resistance pyrometer, as perfected by Callendar and Griffiths, gives wonderfully accurate readings within certain limits. For use both in the laboratory and in the factory it does not seem as popular—in the United States at least—as the Le Chatelier thermo-electric couple. The very accurate work of Messrs. Heycock and Neville is perhaps as good a recommendation for the possibilities of the electrical resistance pyrometer as can be cited. The particular advantages of the thermo-electric couple as applied to alloys research are—its accuracy at high temperatures, its ability to be used with very small masses of heated substances, and, indirectly, its ability to be used in conjunction with a photo-autographic recorder, as has been

so well demonstrated by Sir William Roberts-Austen.

Crystalline Growth in Metals.—Before we enter upon the consideration of alloys, it may be well to note a few general properties of metals, particularly the mode of crystalline growth and the effects of strain. To both of these subjects Professor Ewing, of Cambridge, has given much attention and has explained the phenomena of these operations very clearly. He states that all solid metals are crystalline, even though when examined by the microscope the individual crystals or crystalline grains may not present a simple geometrical outline. The essential point is that the particles composing the mass of a crystal lie in one direction, i.e., have the same plane of orientation. Mr. G. T. Beilby read a paper at the meeting of the British Association held in Glasgow, September, 1901, upon "The Minute Structure of Metals," and cites evidence to show that he has identified minute spicules or scales showing remarkable uniformity of size and appearance in metals of all the leading groups. These under mechanical treatment may be converted into transparent glass-like substance and may again reappear as spicules unchanged in size. The diameter of the scales is estimated to range from 1-300 to 1-400 of a millimeter. The metals examined by Mr. Beilby included gold, silver, platinum, cobalt, nickel, chromium, iron, copper, lead, bismuth, antimony, tin, cadmium, magnesium, aluminum, zinc and sodium. Brasses and bronzes were also examined. The author says that the crystalline faces and cleavages of such metals as antimony, bismuth and zinc exhibit the same features as the softer and more malleable metals, being covered with a film of transparent metal, while in fractures at right angles to cleavage planes, scales are distinctly seen. Mr. Beilby's conclusions are: "The persistence of these minute scales or spicules under all kinds of mechanical and thermal treatment, the remarkable uniformity of their size and appearance in metals

of all the leading groups, their disappearance into the transparent form and their reappearance again, apparently unchanged in size or otherwise, seem to afford fair ground for the conjecture that they are in some way definite units in the structure of metals."

It may be that these are the "units" whose arrangement in certain definite orders constitute crystals, and this similarity of disposition of particles is what constitutes orientation. Professor Ewing explains crystallization in metals in this way: the formation of crystals must be assumed to start simultaneously at many points. The crystals grow until they touch one another, and, although individual crystals are similar, it is not necessary that the corresponding axes of any two of them lie in the same plane. No doubt each crystal is of perfect form so long as it is free to grow in all directions; when the crystals touch, their symmetrical growth is hindered, but the orientation of the subsequent particles which attach themselves is not changed. It is for this reason that orientation rather than geometrical outline is considered the essential feature of crystalline growth. In the case of commercial metals, more or less impure, the impurities are cast out by the growing crystals, and being in fact alloys of the admixed metals with the still fluid principal metal, they have a lower melting point than the pure metal. Therefore, they solidify last and form an investing cement which holds together the primary crystals.

The Effect of Strain.—When a polished metal is subjected to strain there is no change noticeable until the stress exceeds the elastic limit. When, however, the plastic stage is reached, there will appear dark lines more or less perpendicular to the direction of stress. This, Professor Ewing says, is not due to fissuring, for by changing the direction of the rays which illuminate the specimen under observation for vertical to oblique, it will be seen that the erstwhile dark lines appear light,

while the background has changed from light to dark. Fissures would not have reflected light in any case; the permanent elongation is due to slipping of the components of the crystals past each other. That is, the surface which was originally plain, presents, after stress has been applied beyond the elastic limit, the appearance of minute steps. It is as though one should take a pack of playing cards with their ends presenting a smooth surface. Now if the thickness of the pack of cards were one inch, and the pack were bent, the end surface of the pack would measure more than an inch and would consist of little steps, not only the ends, but also a part of the flat surfaces of the cards being exposed.

In the case of metals, the slip-lines need not necessarily lie in one plane. As many as four sets of parallel slip lines have been noticed by Professor Ewing. Mr. William Campbell worked upon this phenomenon independently at about the time that Professor Ewing was making these interesting observations. He experimented with tin, while Professor Ewing worked chiefly with lead, and it is interesting to note how completely their results agree.

The growth of crystals from a solidifying molten mass is easy to comprehend, but why is it that crystals grow in a solid mass of metal not only by annealing but even at ordinary temperatures? Big crystals actually consume the little ones. A bit of rolled tin which was allowed to stand for eighteen months at ordinary temperatures in the laboratory showed a marked change in appearance, due to growth of its crystals. If a specimen of tin is put upon a hot plate and heated to, say, 200° C. for ten days, a growth such as is shown in Fig. 1 is obtained, which shows the tin before and after annealing. This photograph is one of Mr. Campbell's, and is a little under actual size. It also shows very well the different orientation of the crystals. In fact, the growth of these crystals

was so rapid that a microsection through them reveals slip-lines, probably due to this rapid growth. The fact that the slip lines are only parallel within the same crystal seems to confirm this view, for, had the stress been applied longitudinally by artificial means all the slip-lines would have been more or less normal to the direction of the stress.

With regard to the growth of crystals in strained metals when they are subsequently warmed, Mr. Rosenhain has offered this explanation: In strained metals the layer of enveloping alloy surrounding the separate crystals becomes broken, and the dif-

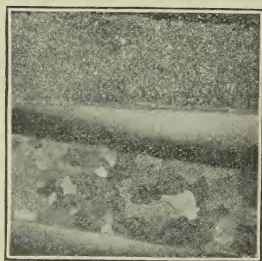


FIG. 1.

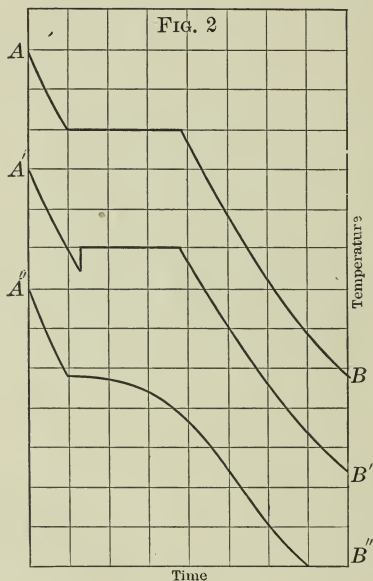
ference of potential between the metal and the alloy set up by electrolytic action causes a solution of the crystal on one side of the alloy and a deposit on the adjoining side. This he verified by the following experiment: Two pieces of lead were scraped clean and welded by the application of great pressure. A micro-section through the weld showed that the crystals in neither piece extended across the weld. When, however, between two such surfaces a little powdered tin was sprinkled and pressure applied, a micro-section revealed that electrolytic action had taken place and that crystals from either side extended across the weld. Ingenious as is this explanation, yet I am not certain that the proof is conclusive. If I mistake not, at

the last Cantor lectures before the Society of Arts,¹ Roberts-Austen and Rose showed crystals of gold extending across a weld, although the purest standard gold was used in the experiment. In fact, long annealing of this gold obliterated the weld almost completely.

Freezing Point of Metals.—With water and many other liquids we know that it is quite possible to lower the temperature to a considerable amount below their freezing-point without the separation of any solid. On the other hand, it is not known that any solid may be heated above its melting-point without becoming liquid. The property first mentioned is known as surfusion. On account of this phenomenon it would be theoretically preferable to determine the melting rather than the freezing point of metals, but practically this is a very difficult task, while freezing-points are in most cases easily determined and surfusion need not interfere with their accuracy in the least, for when solid matter begins to separate from a pure liquid thus cooled, the temperature rises rapidly to the true freezing point and remains constant until the whole mass is solid. Sir William Roberts-Austen cites an instance in which tin was cooled 20° C. below its freezing point without solidification, and I have frequently observed the same result in tin and some other metals, but to a less degree. In working with metals the first point at which solids separate is taken as the freezing point, and surfusion need not obscure this point, particularly if an autographic record of the cooling curve is taken. If we plot a typical cooling curve of a pure metal, using temperature and time as the co-ordinates, we obtain a curve represented by A B, Fig. 2, having two very distinct angles, while a portion is horizontal, i. e., the temperature remains constant during the whole period of solidification. If surfusion takes place, and it is more common in pure metals than in alloys, the curve A' B' represents

(¹) J. Soc. of Arts. (1901) p. 851.

what happens. The temperature falls below the real freezing point, and then rises abruptly to that point and remains constant as in $A B$ until solidification is complete. In impure metals—and since the impurities are usually metallic, they are really alloys—the temperature does not remain constant at all, but a decided change in direction is noticed as shown in $A'' B''$. The greater the amount of impurity, the more rounded will appear the cool-



ing curve. Since these are really the curves of alloys and solid solutions, they will be explained at greater length subsequently. This third type, $A'' B''$ is introduced here because it shows that the nature of the cooling curve gives us a clue as to the purity of the metal under examination. To explain surfusion, we need only remember that fusion is always attended by absorption of heat and solidification by evolution of heat. When a "sur-

fused" substance begins to solidify it disengages heat and the temperature rises until the melting point is reached. No further rise takes place because at this temperature only, liquid and solid are in equilibrium. Any further change of liquid to solid or solid to liquid must be effected by abstracting or adding heat. In practice, either heat is lost by radiation and the whole mass solidifies, or is supplied by artificial warming, and the whole mass becomes liquid.

Binary Alloys.—Having now noted some of the properties of pure metals we may next consider what happens when two metals are melted together. We shall not at this time consider ternary or more complex alloys. The first thing noticed upon melting together two metals is that (1) they mix in all proportions, or (2) they do not. In the first instance, under proper conditions an approximately homogeneous solid mass is likely to result when the molten alloy is cooled. In the second case, on cooling it will be found that the metals have separated into layers, the lighter metal on top. Each layer, however, will be found upon analysis to contain a certain amount of the other metal in solution, just as ether and water dissolve small quantities each of the other. As between certain metals and solid non-metallic elements it seems as though they were absolutely insoluble in one another at ordinary temperatures, although they may be quite soluble at high temperatures. For example, M. Moissan tells us that metals of the platinum group readily dissolve several per cent of carbon at the temperature of the electric furnace, but cast it *all* out as graphite on cooling. It has not yet been determined whether the graphite, which separates in cast iron, contains iron or not. It seems to me that we shall come nearer the truth if we consider such cases as solutions of almost infinite dilution, rather than as absolutely pure metal or non-metal.

We have just spoken of metals dissolving metals, and it is this conception of alloys as solutions—

solid solutions—that has been steadily progressing in favor in recent years and which we hope both to explain and to confirm by citing the results of the experiments of many investigators. I remember hearing a teacher, after explaining the nature of the elements and their tendency to combine in definite propositions, assure the pupils that “alloys are alloys”—a delightfully simple statement, but future pupils as well as their teachers will be expected to know a little more about them.

Very striking analogies exist between ordinary solutions and alloys; in fact, to point out these similarities is to give our present conception of the constitution of alloys. (Van't.)

Solid Solutions.—This expression is due to Vant Hoff, but Roberts-Austen has done most to make it familiar to metallurgists. Our text-books upon physical chemistry contain much information upon the subjects of solutions of gases in liquids, liquids in liquids, and solids in liquids, but are for the most part silent upon the subject of the solutions of solids in solids. The extension of our knowledge upon this subject is very recent and mostly confined to technical periodical literature of recent dates. Professor Roozeboom and his pupils have carried on researches upon the nature of fused mixtures of salts and their behavior upon cooling. This work throws considerable light upon the problems of chemical equilibrium in alloys. As defined by Sir William Roberts-Austen a solid solution is “a homogeneous mixture of two or more substances in the solid state.” In metals no one has worked as yet with non-crystalline mixtures, and solid solutions of metals when crystalline are solid “isomorphous mixtures,” or “mixed crystals.” The use of these three terms to denote one condition is confusing and unnecessary, and as objections exist to the last two synonyms, their use should be discontinued. The term “mixed crystals” is particularly apt to convey a wrong impression to one who sees this name for the first

time, especially if it is unaccompanied by a definition or explanation.

Mr. Stead, in the *Journal of the Iron and Steel Institute*, 1900, classifies solid solutions as follows:

(1) Those in which one constituent of an alloy in crystallizing retains a portion of the other homogeneously diffused through its whole crystalline mass.

(2) Those in which during crystallization the central portion of the crystals contains less of the dissolved substance than their external boundaries.

(3) Those in which the metals form a definite compound, which is retained in solid solution in the excess of metal or metals. I should like to add that the "compound" may be the "solvent," in the sense in which those terms are here used.

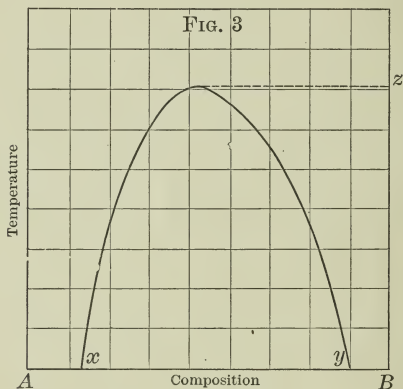
The condition described in (2) is that of an unstable system. Crystallization has taken place more rapidly than diffusion, and in such cases where crystals are not of uniform composition from center to outside complete homogeneity could probably be obtained by annealing. Mr. Stead adds a fourth class.

(4) Those in which the non-metallic elements form definite compounds with a portion of the dissolving metal that remain in solid solution. This class would include the property of metals, such as iron and copper, to dissolve a portion of their oxides. Such solutions have been little studied.

In the case of metals which do not mix in all proportions, the two layers formed on cooling consist of solid solutions belonging to one of the types just mentioned. Some of the pairs of metals which do not mix in all proportions at ordinary temperatures are Zn-Pb, Zn-Bi, Pb-Al, Bi-Al, Cd-Al. These have all been studied by Dr. Alden Wright,* and Mr. Campbell and myself have repeated and verified a part of Dr. Wright's work upon the aluminum alloys. In all these pairs of metals the relative solubility is a function of the temperature;

*(*Proc. Roy. Soc.* 1898-1893)

therefore, it appears likely that at some temperature solubility is complete. Accordingly we may represent the condition existing between these and any other similar pairs of metals by a "critical curve" (Fig. 3). A and B are the metals which are not entirely miscible at ordinary temperatures, but which form layers. The metal A contains the quantity of B represented by the space A x on the composition line. Similarly the metal B contains B y per cent of A. With increasing temperature the mutual solubilities increase, and at a temperature z there is but one solution. Alloys represented by percentage compositions, which fall outside the



curve x z y are homogeneous. Those whose composition is represented by percentages within x z y may be considered as similar to emulsions at all temperatures below the curve at which they are liquid. They are incapable of remaining homogeneous. To such alloys, Sir George Gabriel Stokes gives the name of *ideal* (i.e., unreal, imaginary) alloys while those falling outside the area x z y he calls real alloys. The distinction between such pairs of metals as form separate layers on cooling, and the more or less laminated or striated structure produced upon solidification of eutectic alloys, will be pointed out later.

Molecular Freedom in Solids.—It must not be supposed that because certain bodies are designated "solid" that entire absence of molecular mobility is implied. Such an idea is far from the truth; the difference in mobility of the molecules in "solids" and "liquids" is one of degree only. On the boundary between solids and liquids substances are said to be viscous or plastic. Just as crystals of a soluble salt placed in contact with water tend to become dissolved and uniformly distributed throughout the solvent; so metals, even at normal temperatures, tend to form uniform solutions; this tendency, though slight, is none the less real. Metals even tend to evaporate and to be surrounded by their own vapor. Robert Boyle thought that "even gold" had its "little atmosphere." From analogy with salt solutions we may suppose that one metal dissolved in another shows a small expansive tendency to escape from solution; in other words, exhibits osmotic pressure.

Professor W. Spring, of Liege, demonstrated the fluidity of solids, if I may use that expression, in his famous experiments upon the behavior of metals under exceedingly high pressures—ten thousand atmospheres, more or less. He showed that by pressure alone:

(1) Metals can be made to flow. The familiar operation of striking coins illustrates this property of metals and alloys. A medal has recently been struck in steel.

(2) Solids, both metals and salts, like liquids and gases, possess perfect elasticity and suffer no permanent diminution in volume by pressure. Strain, torsion or bending may produce permanent deformation in a metal or alloy, but there is no limit of elasticity in regard to diminution in volume, for when the pressure is removed the solid assumes its original volume. An exception to this is cited by Professor Spring in his next generalization, viz.:

(3) Allotropic changes may result from pressure.

Prismatic sulphur becomes octahedral sulphur and amorphous arsenic becomes crystalline. In both these cases the second allotropic form is denser than the first, and from these and other experiments Professor Spring argues that allotropic transformations by pressure show that matter takes the state which corresponds to the volume it is obliged to occupy. Moissan's brilliant experiments upon the production of artificial diamonds illustrates this principle.

(4) Metallic filings are converted by pressure alone into solid masses, just as if they had been fused. Similarly mixed filings yield alloys; e.g., brass was produced by compressing clean, flat surfaces of zinc and copper. Reactions of double decomposition between dry salts and the production of the highly colored regulus of Venus (Cu_2Sb) show that not only intimate agglutination, but also chemical combination may take place between bodies in the solid state. I have confirmed some of Professor Spring's results, but was unable to produce several typical intermetallic compounds as Au Al_2 , Sb Sn , Sn Cu_4 , etc.

Professor Roberts-Austen has demonstrated the fact of molecular mobility among solids in a prolonged series of very beautiful experiments upon the diffusion of gold into lead at temperatures from 250°C . down to the ordinary temperature. Graham showed long ago that gold diffusing into molten lead, tin, etc., obeyed Fick's law,

$$\frac{d v}{d t} = K \frac{d^2 v}{d x^2}$$

where x is the distance through which diffusion takes place (against gravity), v is the concentration of the diffusing metal, t = time, and k is the diffusion constant, i.e., the quantity of metal in grams diffusing in unit of area (1 cm^2) in unit of time (1 day) when unit difference of concentration (in grams per cm^3) is maintained between the sides of a layer 1 cm. thick.* That is,

*See Roberts-Austen, Graham Lecture before the Philosophical Society of Glasgow, 1901.

metals dissolve in metals, just as salts dissolve in water. Were it not for the operation of this law it would not be such an easy matter to prepare homogeneous alloys. For instance, with relatively little stirring and relying upon diffusion, it is very easy, according to Sir William Roberts-Austen to make 1,200 ounces of coin gold alloy, the first and last pourings of which shall not differ by more than 1-10,000 part in fineness. The idea that interchange of matter can take place between solids is not a new one, as is shown by the cementation process of the ancient Hebrews by which gold was purified.

The experiments upon the diffusion of gold into solid lead, which Roberts-Austen has recently reported to the Royal Society, may be summarized as follows:

Gold placed in the bottom of a tube filled with lead and maintained at 250° C. (79° below the melting point of lead) appeared at the top in notable quantities in a month. At 100° C. the rate of diffusion was 1-100,000 of that in fluid lead, and in solid lead at the ordinary temperature, allowed to stand in contact for four years, unmistakable signs of diffusion took place, but its rate was such that in one thousand years the diffusion would equal that taking place in one day in lead just molten.

The figure 4 shows another sort of change which may take place in solid materials. An alloy containing 88.7 per cent Cu and 11.3 per cent Al. corresponds closely to the compound Cu_3Al . It should, therefore, appear almost homogeneous, and so it does when quickly cooled. When slowly cooled, however, it changes at 500° C., or nearly 600° below its freezing point, and presents the variegated appearance shown in Fig. 4, which no metallographist would care to call a typical structure for an intermetallic compound.

We apply practically the phenomenon of molecular mobility in solids in all annealing operations.

By this means the ill effects of strain due to sudden cooling are remedied, and equilibrium is established in articles of metal, glass, enamel and other materials. The rate of diffusion of gold in lead at the various temperatures is an indication of the rapid increase in molecular mobility which results by very moderate increments in temperature. This knowledge is applied whenever we resort to moderately elevated temperatures in all sorts of annealing operations. Steel is very sensibly annealed at

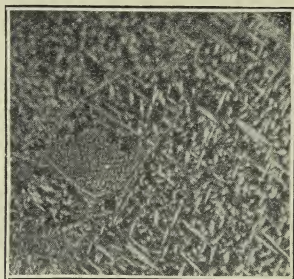


FIG. 4.

temperatures as much as $1,000^{\circ}$ C. below its melting point.

Behavior of Binary Alloys During Cooling from Fused State.—It has been stated that metals may or may not mix in all proportions. If they do mix, we may further distinguish those cases in which (1) chemical combination does not take place, and (2) those in which chemical combination does take place, and one or more intermetallic compounds result. The reality of the existence of intermetallic compounds is undoubted, yet, so far as I know, no mention is made of them in the standard books on general chemistry. Indeed very little is known in regard to the nature of the affinity between metals. It does not seem necessary to suppose that the laws applying to combinations between elements or radicals which are relatively electro-positive and electro-negative be equally applica-

ble here; and our conceptions of valency are seriously shattered if we attempt to reconcile them to intermetallic compounds. The difficulties in studying intermetallic compounds are very great, because they are troublesome to isolate, and in many of their properties they resemble the metals. Frequently, too, they are quite unstable and show marked dissociation. Chemical methods of studying them are of very limited application; filtering off solidified intermetallic compounds from a still fluid metallic mother liquor at high temperatures presents extreme difficulties and volatilization of the excess of solvent metal is rarely applicable. In a few cases the heat of formation can be determined and electrical methods by which the potential of binary alloys is compared with that of the more positive metal in the alloy may yield important evidence as to the solubility of one metal in another in the solid state. The microscopic evidence and that of the freezing point curves require some amplification, for they are not wholly satisfactory in this regard. (See Herschkowitz,, *Zeits. Phys. Chemie*, XXVII., p. 113, and Laurie, *Trans. Chem. Soc.* (1888), p. 104.) One great difficulty in studying intermetallic compounds by chemical means is that even if definite crystals can be isolated from an alloy by using suitable solvents it is found that their compositions vary according to the percentage composition of the alloy from which they were obtained. Apparently identical crystals isolated from alloys of different composition, though of the same crystalline form, will usually differ on analysis. In other words, crystals need not be composed solely of a definite intermetallic compound. This seems to have been the general idea, however, in times past and every worker who succeeded in isolating definite crystals from an alloy promptly assigned to them a formula. Unless a compound is indicated by the appearance of a summit in the freezing-point curve, and unless the alloy corresponds in percentage composition exact-

ly to this summit, it is more than likely that the crystals isolated, though isomorphous with those of the compound, are not of exactly the same composition. This, in general, no doubt accounts for the "discoveries" from time to time of possibly ten Al-Cu compounds and nearly as many Al-Mo compounds of the types $R_xR'_y$, where x and y may be any number from one to twenty. To the same category belong the numerous carbides of iron. I have discovered six in the literature, but not in iron, the existence of all but one of which is denied. For this very reason, namely, the improbable existence of most of the intermetallic compounds mentioned in technical literature of the past ten years, I hesitate to give the formula, $W Al_7$, to some beautiful hexagonal crystals, which are so refractory that neither aqua regia, nor aqua regia and sulphuric acid, nor fused sodium carbonate scarcely attacks them, and whose composition agrees very closely with that formula.

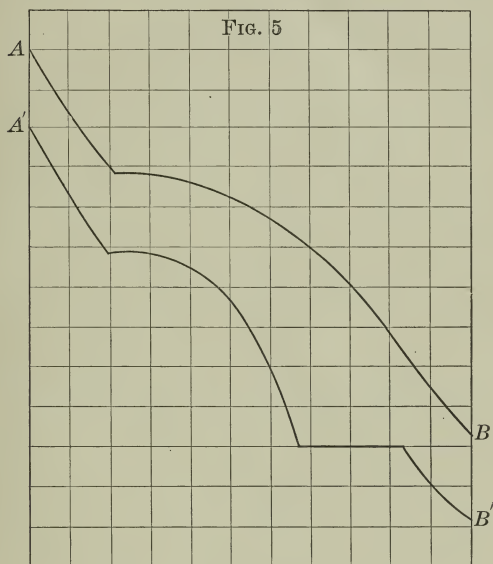
Cooling Curves.—During the cooling of a molten alloy, various constituents may crystallize out successively; definite compounds which are stable only at high temperatures may split up into simple constituents; or, new combinations, impossible at high temperatures, may be formed as the temperature falls. All such molecular changes are accompanied by corresponding thermal effects, such as the disengagement or the absorption of heat. By the accurate measurement of the temperature at which these changes take place we obtain most valuable information in regard to the molecular movements in the mass. The Le Chatelier pyrometer used in conjunction with an auto-photographic recording device seems best suited to measure and record these changes. The general principles of thermoelectric pyrometry are too well known to require discussion here. For reference, however, I could not do better than to refer to H. Le Chatelier and O. Boudouard's volume, "Mesure des Températures Elevées," or to its English translation with supplement by George K. Burgess.

The instruments used by Sir William Roberts-Austen in his private laboratory have been described fully in the *Reports of the Alloys Research Committee* of the Institution of Mechanical Engineers. During several months that it was my privilege to work in his laboratory I made use of a recorder designed by Dr. Stansfield and constructed by the Cambridge Instrument Company. For a description of this, with illustrations, see the *Journal of the Franklin Institute*, January, 1902. Neither of these forms of recorder is perfect, and many improvements will be required to produce an instrument that is entirely satisfactory. Fortunately it is not the accuracy of these instruments, but certain inconveniences of manipulation that are at fault. In using any thermocouple, with or without a recorder, it is necessary to calibrate frequently. The temperatures usually taken as "fixed points" are the boiling points of water (100°), naphthaline (218°), mercury (356.7°), and sulphur (444.5°); the melting points of tin (232°), lead (329°), aluminum (655°), gold (1064°), and copper (1083°). Not all of these need be determined for a single calibration; three or four points if determined with great accuracy will suffice. Other points may be determined by way of verification, and it is convenient as well to have a large variety of materials to select from so that for any special work the curve may be calibrated by means of substances whose melting or boiling points lie near the temperatures at which we desire to operate. For instance, one would not ordinarily use the temperatures 100° , 218° and 232° in constructing a curve for use above 1000° , but would choose 655° , 1064° and 1083° , or other temperatures in this region which are well established as the melting point of potassium sulphate (1084°), or sodium carbonate (850°).

In using the thermo-couple to obtain a cooling-curve of a metal or alloy it is only necessary to insert the couple, suitably protected by a fire-clay or porcelain tube, into the molten mass. A current of electricity is generated whose electro mo-

tive force is approximately proportional to the temperature, or rather the current gives us a measure of the difference in temperature between the hot and cold junctions of the couple. If now this current be passed through a reflecting galvanometer, the beam of light moves rapidly from left to right until it attains a deflection proportional to the temperature measured. This beam of light falls upon the scale which has been calibrated by the establishment of certain fixed points as just explained. If the beam passes through a narrow horizontal slit in a recording device, behind which a photographic plate is rising or falling at a uniform rate, we obtain a cooling-curve whose co-ordinates are time and temperature. The type of curves given by a pure metal, by surfusion and impure metals has already been shown in Fig 2. Two other classes of alloys give a cooling-curve identical with that of a pure metal, viz.: eutectic alloys and intermetallic compounds, that is these three classes of substances freeze at a single temperature. The nature of a eutectic will be discussed later; suffice it here to define it as that alloy of a series which has the lowest freezing-point, which is constant in composition, and which is not a chemical compound of the metals which compose it. In Fig. 5, the curve A B represents that of a homogeneous solid solution. It shows but one "break," though the temperature does not remain constant during the whole period of solidification, as in the case of pure metals, compounds and eutectics. In A' B' is shown a curve with two "breaks," the upper one resembling that of a solid solution and the lower one shows the form of eutectic. The first abrupt change in direction in either of these curves indicates the temperature at which solidification begins. As the excess of one metal solidifies the concentration of the residual fluid is increased with respect to the metal which is not in excess. The ultimate cause of the change in direction is the liberation of the latent heat of solution or of fusion.

As is well known, when concentrated hydrochloric acid (solution of hydrochloric acid gas in water) is boiled, the hydrochloric acid gas evaporates faster than the water. If dilute hydrochloric acid is boiled, the water evaporates relatively faster than the gas. The inevitable result is



that at a certain concentration hydrochloric acid and water vapor leave the liquid at a rate proportional to their concentration; thereafter the composition of the liquid remains constant and the boiling point fixed.

A somewhat analogous condition is that of the solidification of two metals, M and N. Either of them may be considered as the solvent. If M is the solvent and N the dissolved substance, then on cooling such alloy, M crystallizes first retaining some N in solid solution. Similarly an alloy containing much N and little M begins to solidify by the separation of crystals of nearly pure

N containing M in solid solution. As M or N begin to separate out in solid form the remaining liquid portions become concentrated in respect to N and M respectively. The freezing-point of the remaining liquid is thus continually lowered. Eventually either of these classes of alloys reaches a concentration greater than that of a saturated solid solution and then there crystallizes out simultaneously two solid solutions, one of which is a saturated solid solution of M in N and the other a saturated solid solution of N in M. In any one series of metals this takes place at a definite fixed temperature which is the lowest freezing point in the series and no matter what the original composition of the alloy, the part solidifying at this constant temperature is uniform in composition. This is the "eutectic" alloy; it will be considered more fully later in this paper.

Some students of alloys consider that at temperatures between the first separation of solid and the point at which the residue solidifies as a whole, there does not exist a homogeneous condition in the still liquid portions. They liken alloys within this range to an emulsion, or conjugate solutions, etc., simply because ultimately the mass solidifies in a banded or laminated mass characteristic of eutectics. It is not necessary, however, to consider that the two solid solutions constituting the ordinary eutectic existed as such in an emulsified state above the eutectic point. To be sure, the microscope reveals a very marked separation of the alloy into two constituents (when there is any eutectic), usually with characteristically laminated structure, but these two components show no tendency to separate into layers when the alloy is kept for a long time just above its eutectic point; on the other hand, the magnitude of the eutectic structure is markedly influenced by the slowness of cooling. Furthermore there is always an evolution of heat during the freezing of a eutectic

which is very decided and may well be accounted for by such a marked molecular rearrangement as the formation of a laminated structure from a homogeneous mass would involve, and lastly, we might cite some concrete evidence on this point which was brought to my attention by Mr. William Campbell. As is well known the constituent of steel known as martensite which is a solid solution of iron carbide in iron is capable of splitting up at about 690° C. or nearly 800° C. below its freezing-point into the beautifully characteristic structure known as pearlite; accompanying this change is a marked evolution of heat, the critical point A_{r1} of Osmond. If such a decided transformation can take place in solid steel, it surely ought not to be thought improbable that a similar one could take place in an alloy at the instant of final solidification when the molecular freedom of the particles is doubtless many times as great as in the example cited.

Molecular Depression of the Freezing-Point of Metals.—In 1889, Prof. Ramsey determined the molecular weight of many of the metals by the method of measuring the change in vapor pressure when certain known weights of solid metals were dissolved in mercury. He also made determinations at the boiling point of mercury. From these experiments he states "that it would appear legitimate to infer that in solution, as a rule, the atom of a metal is identical with its molecule."

Messrs. Heycock and Neville found that when two metals were melted together, considering M as solvent and N as the dissolved metal, then

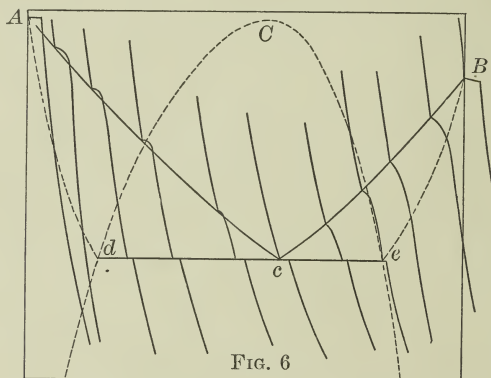
(1) The freezing-point of M is lowered,—the most frequent result.

(2) The freezing-point of M is raised, e. g., silver in cadmium, and antimony in tin.

(3) The freezing-point is unchanged, e. g., thallium in lead, and, I believe, within narrow limits, silver in gold.

But these skillful investigators, to whom we are

so much indebted for their careful researches upon alloys, went further and showed that none of these cases contradicted Van't Hoff's theory of solution. This they did in each case by filtering off the part first solidifying. In the first case the more fusible filtrate was found to be richer in the dissolved metal than were the first crystals. In the second instance the crystals were richer in the dissolved metal; that is, the excess of solvent was not first to separate in the solid form but what was probably a definite compound of the two metals having a higher melting point than the metal M, which was assumed to be the solvent. In the third case there was absolutely no separation of the two metals during cooling; that is, the first crystals and the



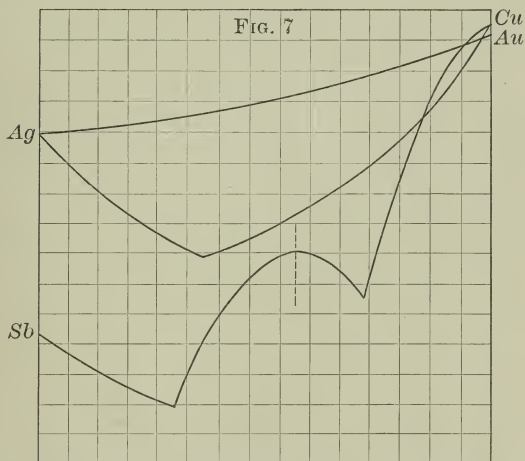
fluid part were identical in composition. That is, the two metals in these instances form isomorphous mixtures. In all their experiments, Messrs. Heycock and Neville were dealing with dilute solutions in which, as in the case of salts dissolved in water, it might be expected that the molecules of the dissolved substance would obey the laws of gases. When their experiments were conducted quantitatively, Heycock and Neville found that two of the empirical laws of Coppey and Raoult hold good for alloys, viz:

(1) For moderate concentration the fall of freezing point is proportional to the weight of dissolved substance present in a constant weight of solvent, and

(2) When the falls produced in the same solvent by different metals are compared, it is found that a molecular weight of a dissolved metal produces the same fall whatever the metal is.

In these experiments tin was the solvent and it was assumed that the metals are monatomic in solution or that their molecules are of one type,— Rn_1 when n is constant and probably equal to 1.

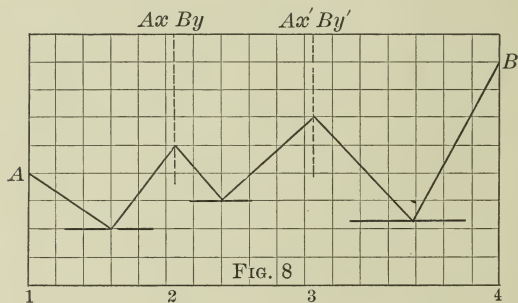
The third law is probably incorrect, for it as-



sumes that if a constant number of molecules of solvent be employed, the fall is independent of the nature of the solvent. The solvent in the case of metals often tends to chemical combination with the other metal. Thus gold in 100 atoms of sodium gave 4° C. depression in the freezing-point; in tin, 3° C. and in potassium only 1.8° C.

Freezing-point Curves.—One must not confuse cooling-curves and freezing-point curves. The

former, as already pointed out, result during the cooling of a single metal or alloy and time and temperature are the co-ordinates of such curves. When a series of such curves are obtained for any pair of metals mixed in all proportions from 0 to 100 per cent M in 100 to 0 per cent N, and the critical points are plotted in a diagram of which the co-ordinates are temperature and composition we get what is known as a freezing-point curve. That is, the points at which all possible combinations of the two metals freeze are indicated more or less accurately. The more points in the curve actually determined, the more likely becomes the accuracy of the other points. Subsidiary points in the cooling-curves may also be plotted, though they are not strictly speaking freezing-



points. Figure 6 is taken from a paper upon "La Constitution des Alliages Metalliques" by Roberts-Austen and Stansfield which was presented at the Physical Congress, Paris, 1900. The vertical co-ordinate is temperature and the horizontal one represents both time (for cooling-curves) and composition (for the freezing-point curve). It shows graphically how a complete freezing-point curve is constructed from cooling-curves. It will be noticed that the metals A and B forming the alloy give cooling-curves of the type of pure metals. In the curves showing a eutectic break, it

will be noticed that the magnitude of the eutectic break as compared with the upper or freezing-point break becomes relatively greater as we approach the composition of the alloy c which is pure eutectic and gives a cooling-curve identical in form with those of A and B. In fact this ratio gives a rough approximation of the proportion of the alloy which consists of solid solution separating at the first break and eutectic alloy crystallizing at the fixed temperature indicated by the horizontal part of the cooling-curve; or, in other words, if the alloy consists mostly of solid solution and a little eutectic, it will take the former longer to solidify than it does the latter and the cooling-curve indicates this roughly. Sometimes more than two breaks occur in a cooling-curve, indicating changes, allotropic or otherwise, occurring in the solid.

Freezing-point curves conform in general to three types, as shown in Fig. 7. These curves are not drawn exactly to scale, but are approximately correct. Gold and silver alloys form perfectly isomorphous mixtures, and their freezing points give almost a straight line joining the freezing points of the pure metals. Copper and silver give the typical curve of two metals, which mix in all proportions, but do not unite chemically. Antimony and copper unite to give the highly colored compound known as regulus of Venus, Cu_2Sb . *This compound is indicated in the cooling-curve by the intermediate summit. In general such a summit will be found to occur at a formula percentage, and indicates an intermetallic compound. To explain such a curve, we have only to consider it as made up of separate sections, as indicated in the figure by a dotted line. The intermetallic compound has a melting point of its own, quite independent of that of the constituent metals. It may be higher, lower or intermediate as com-

*The formula usually given in the past was Cu_5Sb_2 , but Stead says the purple constituent is Cu_2Sb .

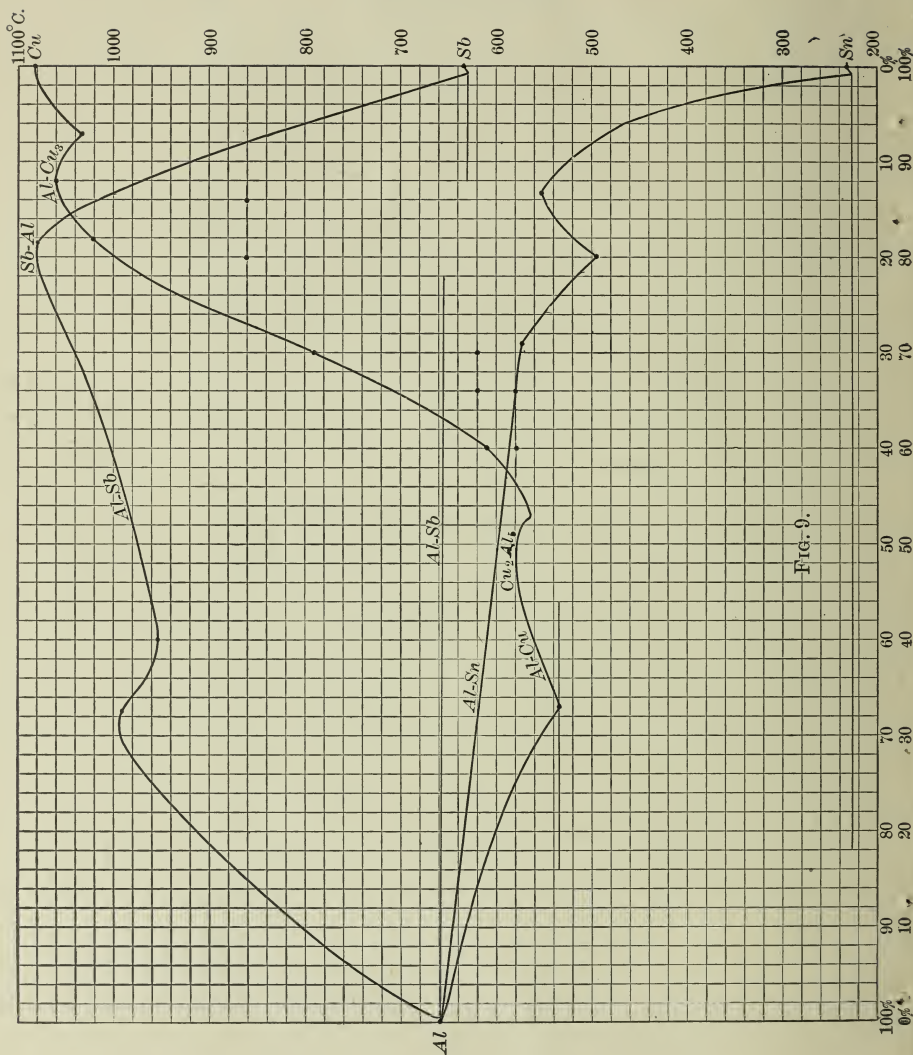


Fig. 9.

pared with the constituent metals which compose it. In such a curve as the Sb-Cu one, we may consider that one series of alloys is composed of mixtures of Sb and Sb Cu₂, and the other of Sb Cu₂ and Cu. We are virtually dealing with two distinct series of alloys, each of which taken separately is of the simple type illustrated by the Ag-Cu curve. In the Sb-Sb-Cu₂ portion of the curve there is no free copper, and in Cu-Sb Cu₂ portion of the curve there is no free antimony. Dissociation of the compound might make some modification of the above statement necessary, and, indeed, it has been suggested that dissociation causes a summit to appear rounded instead of angular. Curves containing more than one summit may be similarly resolved into series of two components, which may be respectively a metal and an intermetallic compound, or, if between two summits, the components are both intermetallic compounds. An ideal representation of such a curve is shown in Fig. 8. In this figure we see that alloys whose compositions fall between 1 and 2 consist of metal A and compound Ax By; alloys between 2 and 3 consist of components Ax By, and Ax' By'—they contain no free A or B; alloys between 3 and 4 consist of compound Ax' By' and metal B. Each of these pairs of components has its melting point depressed by the presence in it of the adjacent component. Our Cu-Al curve (Fig. 9) may be explained in this way: Two summits occur at the compositions corresponding to Cu₂ Al₃ and Al Cu₃ (48.49% Cu, and 87.6% Cu respectively). Le Chatelier thinks he has detected with the microscope at least four compounds. Our curve gives no indication of them. Our own microscopic study of these alloys is not yet completed. Our Al-Sb curve (Fig. 9) shows the presence of a compound whose melting point is more than 400° C. above that of either constituent. Its formula is Sb Al (81.6% Sb). In this series of alloys we are dealing with two pairs of constituents, Al-Al Sb and Al Sb-Sb. The compound seems to be almost insoluble in either of the pure metals, but on theoretical

grounds we should expect to find a slight depression in the freezing point of each metal as indicated in the curve. These points have not as yet been experimentally detected. The tin-aluminum curve shows a fall of 3° or 4° C. by the addition of 0.5% Al, while with increased additions of aluminum the freezing point is raised 300° C. at a concentration of 10% Al, 90% Sn.



FIG. 10.

If in a certain series of alloys we get a cooling curve with a summit occurring at a formula percentage, and examine the alloys whose freezing points give rise to that summit, we shall find that in general an intermetallic compound in the pure state presents under the microscopic a homogeneous mass made up of crystals, all of which are the same. As we de-

scend from the summit on either branch of the curve we find these crystals becoming less and less in number and size, and at the next angle in the curve they disappear entirely. This is illustrated by the accompanying photographs of antimony-aluminum alloys. These microphotographs were made by Mr. Campbell.

Fig. 10.—20 per cent Sb, 80 per cent Al \times 33 diameters, oblique illumination, shows crystals of Sb Al in granular ground mass of nearly pure Al.

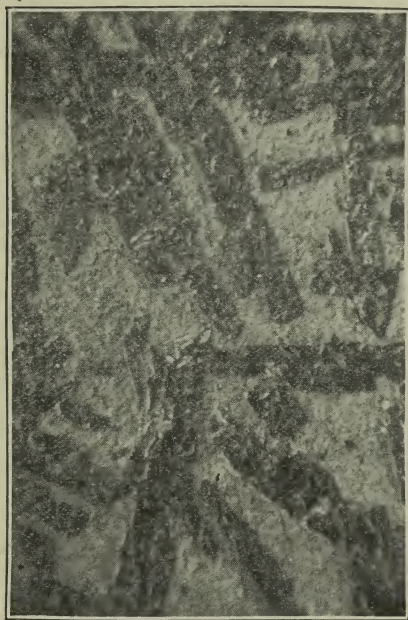


FIG. 11.

Fig. 11.—50 per cent Sb, 50 per cent Al \times 33 diameters, oblique. Crystals of Sb Al increasing in size and amount, ground mass decreasing.

Fig. 12.—82 per cent Sb, 18 per cent Al \times 16 diam-

eters, verticle illumination. This photograph shows nearly pure Sb Al.

Fig. 13.—85 per cent Sb, 15 per cent Al $\times 33$ diameters, vertical illumination. We have passed the summit of the curve; the ground mass of aluminum has disappeared and some free antimony is seen.

Fig. 14.—95 per cent Sb, 5 per cent Al $\times 33$ diameters, oblique. Sb Al crystals diminishing in quantity, and ground mass of Sb—probably containing a little Sb Al in solid solution—is conspicuous.

Regarding this microscopic evidence, supporting

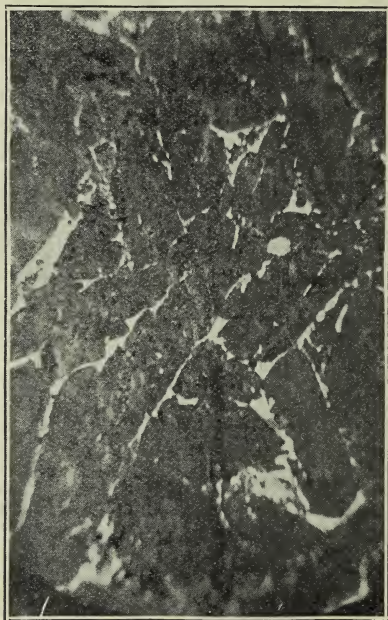


FIG. 12.

the pyrometric evidence, Mr. Neville says: "These criteria taken together, (1) the occurrence of a summit at a formula percentage, (2) the presence of large

crystals of the same kind, decreasing in amount as we descend the branch on either side, are an absolute proof of the reality of a compound."

The Nature of Eutectics.—In several portions of this paper eutectic alloys have been mentioned, a term for which we are indebted to Dr. Guthrie, who used it to designate the most fusible alloy of a series—the one which freezes last. There are certain points in which eutectics may differ, and upon these differences they may admit of classification. Every eutectic, however, possesses the following properties:

1. It is of uniform composition in any one series of alloys.
2. Its freezing point is constant throughout any one series.
3. The freezing point is the lowest in the series.
4. It is not a chemical compound.

The composition of a eutectic may and occasionally does correspond to some simple atomic ratio. This coincidence, though striking, does not prove the presence of a compound as the sole constituent of a eutectic. Usually it possesses a laminated microstructure, and often requires very high magnification to detect the two constituents. Mr. Stead, in his splendid paper upon iron and phosphorus, gives his ideas upon the subject of eutectics, and in addition to what has just been said as to the essentials of a eutectic, he adds some remarks upon what a eutectic may be: (1) "It may consist of two or more metals which do not unite chemically, or (2) of a metal and a definite compound (containing that metal), or (3) possibly of two or more definite compounds. (4) It may consist of a mixture of a solid solution of one metal in another and a free metal. (5) It may contain a solid solution of a definite metallo-metallic salt (intermetallic compound) and that same metallo-metallic salt in the free state. (6) It may possibly consist of two solid solutions." The last of these statements, which he qualified by the word "possibly," seems to me to be the most important of all; and since I am unwilling to admit that any

metal or intermetallic compound ever separates absolutely pure, those conditions in which Mr. Stead speaks of the separation of pure substances seem to me to be inaccurate. The form of the freezing point curves and the explanation of them according to Prof. Roozeboom renders it highly improbable that any strictly pure material separates at the freezing

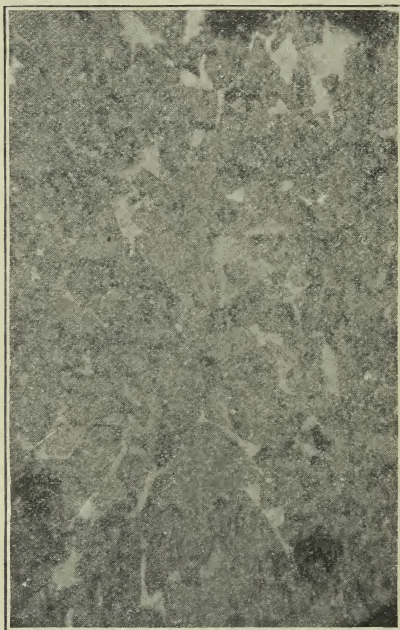


FIG. 13.

point of the eutectic. The most that we can say of the constituents of a eutectic is that in certain cases they are solutions of extreme dilution. In cases where the freezing point curve lies almost entirely above the melting point of either or both constituents, but in which there is a slight depression of the freezing point by very small additions of one metal to the

other, as in the case of tin-aluminum, previously mentioned, and when this depression is further indicated in a well-marked eutectic break in other alloys of the series, it may be possible that the eutectic is a single solid solution. The quantity of dissolved metal in such a eutectic might not be enough to change the type of cooling curve seriously, and probably exceedingly high magnification would fail to resolve such an eutectic into two components, for it crystallizes isomorphously with the pure tin, hence it seems that no two juxtaposed constituents are there. This conception of a eutectic is not at variance with the four essentials already enumerated. While not speaking

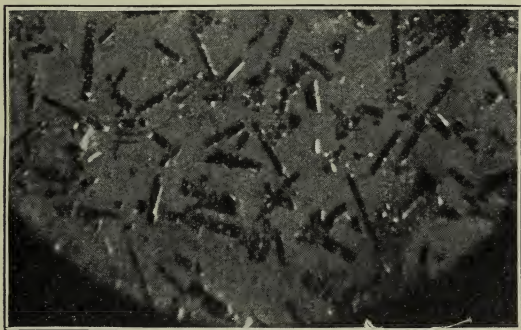
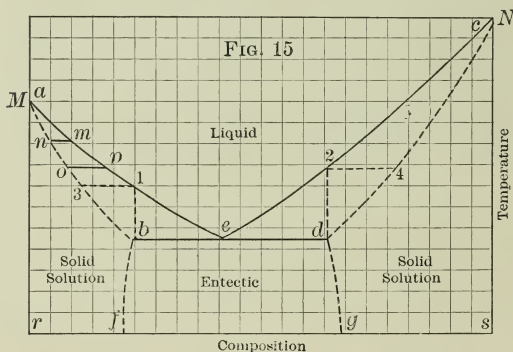


FIG. 14.

positively on this point, I think it reasonable, and am not sure but that in such a curve as the Sb-Sn curve, where all the points seem to lie above the melting point of tin, we must consider pure tin as the eutectic—it melts lowest for the series, it is of constant composition, and it is not a chemical compound.

We have now indicated many points of resemblance between metallic mixtures and ordinary solutions. One metal diffuses into another like a salt into water; like two liquids, they may be perfectly miscible or form layers; the layers are not pure, but each contains a little of the other in solution; in general, the solubility increases with the temperatures. They will

flow under pressure; they may or they may not react chemically when brought into intimate association by fusion or pressure; the molecular mobility increases with the temperature; upon cooling of binary alloys we observe phenomena strongly suggestive of the freezing of salt solutions; the depression of the freezing point of one metal when another is added follows the laws of Coppet and Raoult, and the eutectic reminds us very much of the "cryohydrates" of ordinary solutions. Scarcely another point of resemblance is needed but one is at hand, and a very important one, viz., the phase rule applies quite as well to the explanation of conditions of equilibrium in alloys as it does to the explanation of similar problems in regard to liquid solutions. The classification of the systems, however, requires some modification before the generalizations of Trevor apply, and it is practically somewhat difficult to ensure complete equilibrium in an alloy—the cooling is usually much



too rapid to allow of the establishment of equilibrium in the solid mass. If equilibrium has been established, then the number of distinct substances in the mass will depend upon the number of constituents which enter into the composition of the mass. In my paper already referred to in the *Journal of the Franklin Institute*, February, 1902, I have shown how the

adaptation of the phase rule to alloys is accomplished, and as this is more a chemical conception than one of direct interest to engineers, it need not be dwelt upon here. The phase rule does not tell us the number of phases in which one or two components may exist, but how many of them may exist simultaneously in equilibrium. Thus pure iron may exist in three solid, and one liquid phase, but never in all four at one time. Again the iron-carbon alloys, according to Roozeboom, may exhibit at least seven phases, viz., carbon, α -iron, β -iron and γ -iron, liquid solution, solid solution of carbon in γ -iron, and cementite or iron-carbide. The provisions of the phase rule, however, tell us that only three of these may exist in equilibrium at any given temperature and concentration. Professor Roozeboom's explanation of a freezing-point curve considered as an equilibrium curve is of great interest in helping to make clear the series of phenomena which are exhibited during the actual solidification of molten alloys. His original explanation was given in connection with the highly complicated iron-carbon curves of Roberts-Austen. It has seemed to me that a simpler figure would lend itself more readily to this explanation and the accompanying figure shows the type of curves which gold-copper and copper-silver alloys give, i. e., pairs of metals soluble in each other in all proportions but not forming any compounds. In Fig. 15 the curve *a e c* represents the temperatures at which for each concentration solidification begins. The curve *a b d c* shows the temperature at which solidification is complete. Except for the straight portion of this curve, *b d*, the exact position of it is a matter of conjecture. According to Stansfield, its position may be calculated with some degree of accuracy upon theoretical grounds, if the latent heat of fusion of the solvent is known and assuming that the dissolved substance is monatomic in the liquid state. The upper line, *a e c* Roozeboom calls the "liquid" curve, and the lower line, *a b e d c* he calls the "solid" curve. When in a series of alloys

the liquid and solid curves have a maximum or minimum point formed by the branches of the curve, they touch at this point as in the curve before us. The point in our diagram where the liquid and solid curves meet is the eutectic point. It means that the liquid represented by the composition corresponding to that point solidifies as a whole at a single temperature. Curves similar to this may be used to explain such complicated freezing-point curves as that of the Al-Cu series, remembering that the termini of the liquid and solid curves are not necessarily pure metals, but may be a metal and a compound, or perhaps two compounds. The more or less triangular areas, abe and cde represent mixtures of liquid and solid phases. The areas abr and cdg are solid solutions, and in the area $bdfg$ we have a conglomerate of eutectic alloy, with varying amounts of crystals of solid solution depending upon the composition of the alloy from which they were derived. At the single composition e , however, we have an exception to this statement, for this alloy consists of eutectic only, while to the left of this the conglomerate consists of eutectic plus solid solutions of N in M, and in alloys represented by compositions to the right of e we have eutectic (always constant in composition) plus more or less of a solid solution of M in N.

Above the liquid curve we have only liquid phases; below the solid curve we have only solid phases, while intermediate areas correspond to a mixture of liquid and solid phases.

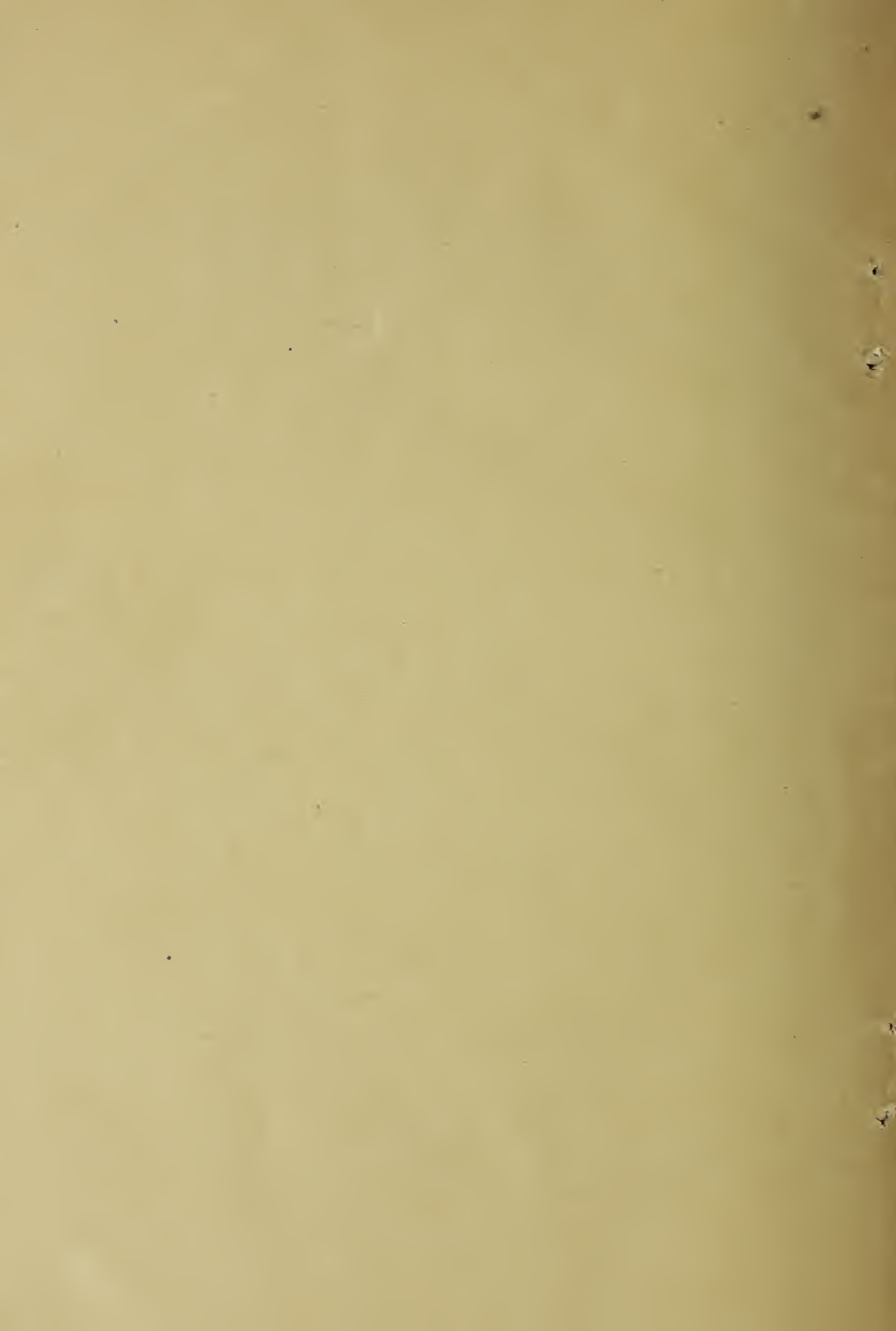
Any alloy whose composition falls within the areas marked solid solution gives but one break in the cooling curve. Alloys represented by compositions falling within the area of the eutectic (except alloy e) give two breaks in the cooling-curves. The eutectic itself consists of two solid solutions, whose compositions are indicated by compositions corresponding to the extreme ends of the eutectic line, viz., b and d . However, since the solubility of one metal in another is a function of the temperature below

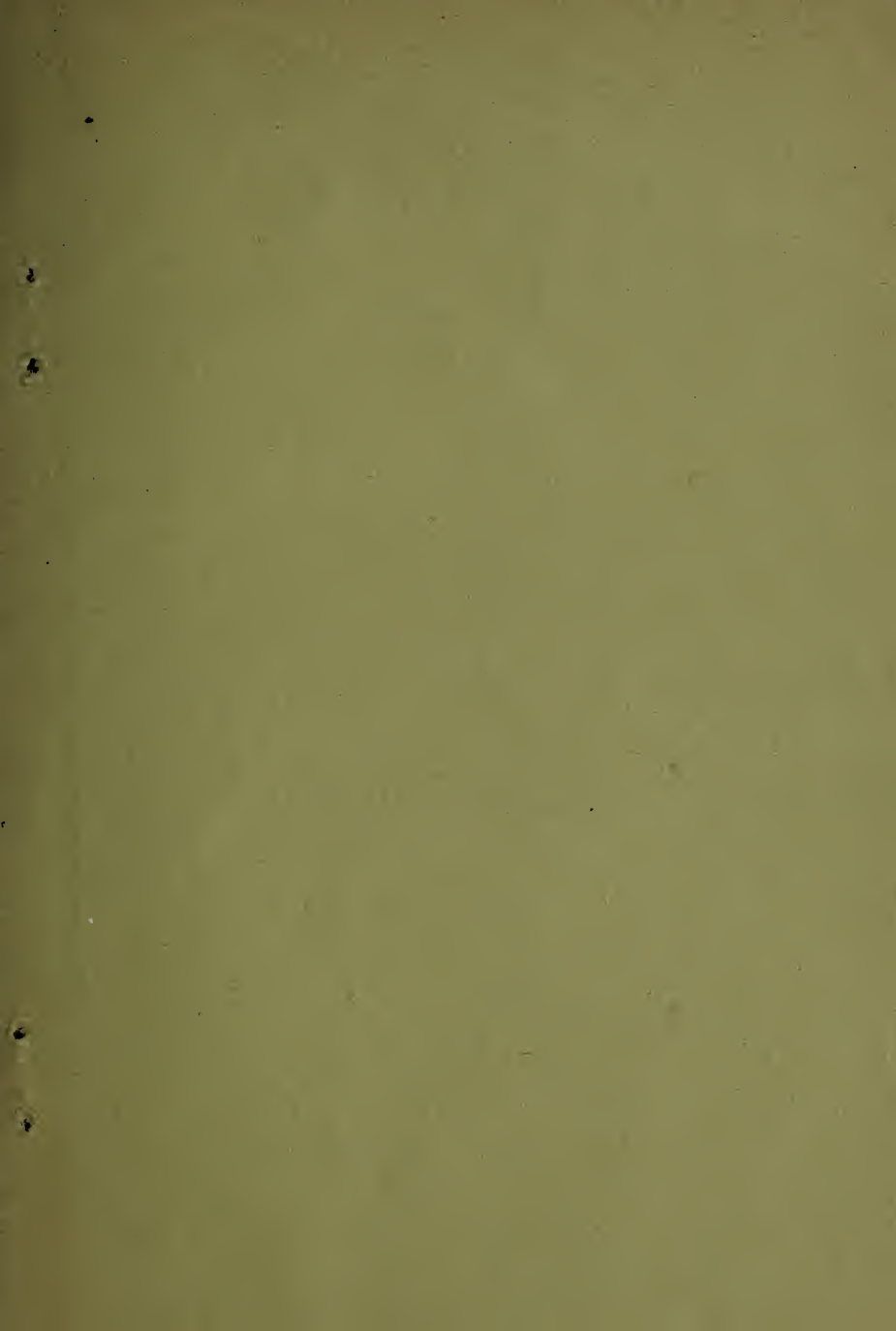
its freezing point as well as above, we may assume that the solubility in the two components of the eutectic decreases slightly even after solidification, and therefore the lines $b f$ and $d g$ are represented as slanting rather than perpendicular to the composition line. These lines indicate the maximum solubility of either metal in the other at temperatures below the freezing point of the eutectic.

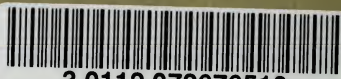
Let us consider the phenomena of solidification of an alloy represented by a composition on $a e$, as explained by Roozeboom. Any solution represented by the composition m begins to solidify at that temperature by the separation of crystals of the composition n . They therefore contain less of N than the liquid alloy m . The residual alloy has therefore become enriched in N, and its freezing point is lowered; its composition passes thus from m to p , at which point solidification is complete, for at this point the temperature has fallen till it encounters the solid curve at the point o . The point o , moreover, indicates the composition of the last crystals to solidify. That is, while the liquid solution is changing from m to p , the composition of the crystals has changed from n to o . Complete solidification has thus taken place through an interval, $m o$. Now there is an alloy whose final solidifying point is b ; and according to Roozeboom's explanation it is an alloy of composition, e , which is freezing. At the same temperature, however, occurs the solidification of the solid solution of composition d . Finally, then, all alloys represented by compositions between 1 and 2, after separating out crystals of solid solutions of N in M, or M in N, represented by compositions along the lines 3, 1 and 2, 4, respectively, become concentrated to the composition e , where saturated solid solutions of compositions b and d solidify side by side, constituting the eutectic. That is, an alloy the vertical projection of whose composition upon the solid curve does not cut the eutectic line, consists of a single solid solution. An alloy whose composition projected vertically intersects the eutectic line, consists of a conglomerate of eutectic of con-

stant composition c and a solid solution, whose composition is represented by the horizontal projection of its composition upon the corresponding solid curve. At temperatures and concentrations lying within the areas enclosed by the liquid and solid curves there exists in equilibrium solid and liquid solutions, e. g., at a temperature and concentration represented on the line $m n$ there exists simultaneously liquid solution m and solid solution n .

Great as has been the progress in alloys research within the past few years, yet much remains to be done. When many sets of complete freezing-point curves have been determined, when all the alloys of these series have been examined metallographically, and when their ordinary physical tests, tensile strength, electrical and heat conductivity, specific gravities, etc., have been accurately worked out, then we may be able to generalize and to predict properties of new pairs of metals as well as to set out intelligently to produce new and useful alloys. It must be admitted that the production of alloys in the past has been by the very wasteful method of chance. I hope to see the manufacture of alloys become an exact science and that ultimately even ternary or more complex alloys may be brought within the range of applicability of "natural laws," which as yet remain undiscovered. We are making progress in the right direction, but American scientists have not yet assumed their due share of this task. It is time that we followed the example of the British association, the Société d'Encouragement pour l'Industrie Nationale, the Institution of Mechanical Engineers and the National Physical Laboratory of Great Britain, in promoting the scientific study of problems in connection with alloys.







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